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(54) Title: PROCESS FOR PRODUCING SINGLE WALL NANOTUBES USING UNSUPPORTED METAL CATALYSTS AND SINGLE WALL NANOTUBES

(57) Abstract

A process for producing hollow, single–walled carbon nanotubes by catalytic decomposition of one or more gaseous carbon compounds by first forming a gas phase mixture of carbon feed stock gas comprising one or more gaseous carbon compounds, each having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions; and then conducting said decomposition reaction under decomposition reaction conditions, thereby producing said nanotubes.

TITLE OF THE INVENTION

PROCESS FOR PRODUCING SINGLE WALL NANOTUBES USING UNSUPPORTED METAL CATALYSTS AND SINGLE WALL NANOTUBES

5

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method for producing single wall carbon nanotubes, also known as
10 linear fullerenes, employing unsupported metal containing catalysts, for decomposition of a C_1 to C_6 carbon feedstock such as carbon monoxide.

Description of the Related Art

Multi-walled Carbon Nanotubes

15 Multi-walled carbon nanotubes, or fibrils, are well-known. Typically, carbon fibrils have a core region comprising a series of graphitic layers of carbon.

Since the 1970's, carbon nanotubes and fibrils have been identified as materials of interest for a
20 variety of applications. Submicron graphitic fibrils belong to a class of materials sometimes called vapor grown carbon fibers. Carbon fibrils are vermicular carbon deposits having diameters less than approximately 1.0μ. They exist in a variety of forms and have been
25 prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Such vermicular carbon deposits have been observed almost since the advent of electron microscopy. A good early survey and reference is found in Baker and Harris,
30 <u>Chemistry and Physics of Carbon</u>, Walker and Thrower ed., Vol. 14, 1978, p. 83, and in Rodriguez, N., <u>J. Mater. Research</u>, Vol. 8, p. 3233 (1993).

Carbon fibrils were seen to originate from a metal catalyst particle which, in the presence of a
35 hydrocarbon containing gas, became supersaturated in carbon. A cylindrical ordered graphitic core is extruded which immediately became coated with an outer layer of

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pyrolytically deposited graphite. These fibrils with a
pyrolytic overcoat typically have diameters in excess of
0.1μ. (Obelm, A. and Endo, M., _J. Crystal Growth_,
32:335-349(1976).)

5   Tibbetts has described the formation of
straight carbon fibers through pyrolysis of natural gas
at temperatures of 950°-1075° C., _Appl. Phys. Lett._
42(8):666(18\983). The fibers are reported to grow in
two stages where the fibers first lengthen catalytically
10   and then thicken by pyrolytic deposition of carbon.
Tibbetts reports that these stages are "overlapping", and
is unable to grow filaments free of pyrolytically
deposited carbon. In addition, Tibbett's approach is
commercially impracticable for at least two reasons.
15   First, initiation of fiber growth occurs only after slow
carbonization of the steel tube (typically about ten
hours), leading to a low overall rate of fiber
production. Second, the reaction tube is consumed in the
fiber forming process, making commercial scale-up
20   difficult and expensive.

          In 1983, Tennent, U.S. Patent No. 4,663,230
succeeded in growing cylindrical ordered graphite cores,
uncontaminated with pyrolytic carbon, resulting in
smaller diameter fibrils, typically 35 to 700 Å (0.0035
25   to 0.070μ), and an ordered "as grown" graphitic surface.
Tennent '230 describes carbon fibrils free of a
continuous thermal carbon overcoat and having multiple
graphitic outer layers that are substantially parallel to
the fibril axis. They may be characterized as having
30   their c-axes, (the axes which are perpendicular to the
tangents of the curved layers of graphite) substantially
perpendicular to their cylindrical axes, and having
diameters no greater than 0.1μ and length to diameter
ratios of at least 5.

35   Tennent, et al., US Patent No. 5,171,560
describes carbon fibrils free of thermal overcoat and
having graphitic layers substantially parallel to the

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fibril axes such that the projection of said layers on
said fibril axes extends for a distance of at least two
fibril diameters. Typically, such fibrils are
substantially cylindrical, graphitic nanotubes of
5   substantially constant diameter and comprise cylindrical
graphitic sheets whose c-axes are substantially
perpendicular to their cylindrical axis. They are
substantially free of pyrolytically deposited carbon,
have a diameter less than 0.1μ and a length to diameter
10 ratio of greater than 5.

Moy et al., USSN 07/887,307 filed May 22, 1992,
describes fibrils prepared as aggregates having various
macroscopic morphologies (as determined by scanning
electron microscopy) including morphologies resembling
15 bird nests ("BN"), combed yarn ("CY") or "open net"
("ON") structures.

Multi-walled carbon nanotubes of a morphology
similar to the catalytically grown fibrils described
above have been grown in a high temperature carbon arc
20 (Iijima, Nature 354 56 1991). (Iijima also describes
arc-grown single-walled nanotubes having only a single
layer of carbon arranged in the form of a linear
Fullerene.) It is now generally accepted (Weaver,
Science 265 1994) that these arc-grown nanofibers have
25 the same morphology as the earlier catalytically grown
fibrils of Tennent. **Single-walled Carbon Nanotubes**

As mentioned above, the Iijima method partially
results in single-walled nanotubes, i.e., nanotubes
having only a single layer of carbon arranged in the form
30 of a linear Fullerene.

United States Patent No. 5,424,054 to Bethune
et al. describes a process for producing single-walled
carbon nanotubes by contacting carbon vapor with cobalt
catalyst. The carbon vapor is produced by electric arc
35 heating of solid carbon, which can be amorphous carbon,
graphite, activated or decolorizing carbon or mixtures
thereof. Other techniques of carbon heating are

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discussed, for instance laser heating, electron beam
heating and RF induction heating.

Smalley (Guo, T., Nikoleev, P., Thess, A.,
Colbert, D.T., and Smally, R.E., Chem. Phys. Lett. **243**:
5   1-12 (1995)) describes a method of producing single-
walled carbon nanotubes wherein graphite rods and a
transition metal are simultaneously vaporized by a high-
temperature laser.

Smalley (Thess, A., Lee, R., Nikolaev, P., Dai,
10 H., Petit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G.,
Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tonárek,
D., Fischer, J.E., and Smalley, R.E., Science, **273**: 483-
487 (1996)) also describes a process for production of
single-walled carbon nanotubes in which a graphite rod
15 containing a small amount of transition metal is laser
vaporized in an oven at about -1200°C. Single-wall
nanotubes were reported to be produced in yields of more
than 70%.

Each of the techniques described above employs
20 (1) solid carbon as the carbon feedstock. These
techniques are inherently disadvantageous. Specifically,
solid carbon vaporization via electric arc or laser
apparatus is costly and difficult to operate on the
commercial or industrial scale.

25   Supported metal catalysts for formation of SWNT
are also known. Smalley (Dai., H., Rinzler, A.G.,
Nikolaev, P., Thess, A., Colbert, D.T., and Smalley,
R.E., Chem. Phys. Lett. **260**: 471-475 (1996)) describes
supported Co, Ni and Mo catalysts for growth of both
30 multi-walled nanotubes and single-walled nanotubes from
CO, and a proposed mechanism for their formation.

However, supported metal catalysts are
inherently disadvantageous, as the support is necessarily
incorporated into the single-walled carbon nanotube
35 formed therefrom. Single-walled nanotubes contaminated
with the support material are obviously less desirable

compared to single-walled nanotubes not having such contamination.

OBJECTS OF THE INVENTION

5   It is thus an object of the present invention to provide a method of producing single-walled carbon nanotubes which employs a gaseous carbon feedstock.

It is an object of this invention to provide a method of producing single-walled carbon nanotubes which

10   employs a gas phase, metal containing compound which forms a metal containing catalyst.

It is also an object of the invention to provide a method of producing single-walled carbon nanotubes which employs an unsupported catalyst.

15   It is a further object of this invention to provide a method of producing single-walled carbon nanotubes which employs a gaseous carbon feedstock and an unsupported gas phase metal containing compound which forms a metal containing catalyst.

20
SUMMARY OF THE INVENTION

The invention relates to a gas phase reaction in which a gas phase metal containing compound is introduced into a reaction mixture also containing a

25   gaseous carbon source. The carbon source is typically a C_1 through C_6 compound having as hetero atoms H, O, N, S or Cl, optionally mixed with hydrogen. Carbon monoxide or carbon monoxide and hydrogen is a preferred carbon feedstock.

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Increased reaction zone temperatures of approximately 400°C to 1300°C and pressures of between ~0 and ~100 p.s.i.g., are believed to cause decomposition of the gas phase metal containing compound to a metal

5 containing catalyst. Decomposition may be to the atomic metal or to a partially decomposed intermediate species. The metal containing catalysts (1) catalyze CO decomposition and (2) catalyze SWNT formation. Thus, the invention also relates to forming SWNT via catalytic

10 decomposition of a carbon compound.

The invention may in some embodiments employ an aerosol technique in which aerosols of metal containing catalysts are introduced into the reaction mixture. An advantage of an aerosol method for producing SWNT is that

15 it will be possible to produce catalyst particles of uniform size and scale such a method for efficient and continuous commercial or industrial production. The previously discussed electric arc discharge and laser deposition methods cannot economically be scaled up for

20 such commercial or industrial production.

Examples of metal containing compounds useful in the invention include metal carbonyls, metal acetyl acetonates, and other materials which under decomposition conditions can be introduced as a vapor which decomposes

25 to form an unsupported metal catalyst.

Catalytically active metals include Fe, Co, Mn, Ni and Mo. Molybdenum carbonyls and Iron carbonyls are the preferred metal containing compounds which can be

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decomposed under reaction conditions to form vapor phase
catalyst. Solid forms of these metal carbonyls may be
delivered to a pretreatment zone where they are
vaporized, thereby becoming the vapor phase precursor of

5   the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a reactor capable of
producing SWNT.

10   Fig. 2 illustrates the vaporizer component of
the reactor described in Fig. 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

It has been found that two methods may be
15   employed to form SWNT on unsupported catalysts. The
first method is the direct injection of volatile
catalyst. The direct injection method is described is
copending application Serial No. 08/459,534, incorporated
herein by reference.

20   Direct injection of volatile catalyst
precursors has been found to result in the formation of
SWNT using molybdenum hexacarbonyl [$Mo(CO)_6$] and dicobalt
octacarbonyl [$Co_2(CO)_8$] catalysts. Both materials are
solids at room temperature, but sublime at ambient or
25   near-ambient temperatures -- the molybdenum compound is
thermally stable to at least 150°, the cobalt compound
sublimes with decomposition "Organic Syntheses via Metal
Carbonyls," Vol. 1, I. Wender and P. Pino, eds.,
Interscience Publishers, New York, 1968, p. 40).

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The second method uses a vaporizer to introduce the metal containing compound (Fig. 2).

In one preferred embodiment of the invention, the vaporizer 10, shown at Fig. 2, comprises a quartz
5   thermowell 20 having a seal 24 about 1" from its bottom to form a second compartment. This compartment has two 1/4" holes 26 which are open and exposed to the reactant gases. The catalyst is placed into this compartment, and then vaporized at any desired temperature using a
10   vaporizer furnace 32. This furnace is controlled using a first thermocouple 22.

A metal containing compound, preferably a metal carbonyl, is vaporized at a temperature below its decomposition point, reactant gases CO or CO/H_2 sweep the
15   precursor into the reaction zone 34, which is controlled separately by a reaction zone furnace 38 and second thermocouple 42.

Although applicants do not wish to be limited to a particular theory of operability, it is believed
20   that at the reactor temperature, the metal containing compound is decomposed either partially to an intermediate species or completely to metal atoms. These intermediate species and/or metal atoms coalesce to larger aggregate particles which are the actual catalyst.
25   The particle then grows to the correct size to both catalyze the decomposition of CO and promote SWNT growth. In the apparatus of Fig. 1, the catalyst particles and

the resultant carbon forms are collected on the quartz

wool plug **36**.

Rate of growth of the particles depends on the

concentration of the gas phase metal containing

5   intermediate species. This concentration is determined

by the vapor pressure (and therefore the temperature) in

the vaporizer. If the concentration is too high,

particle growth is too rapid, and structures other than

SWNT are grown (e.g., MWNT, amorphous carbon, onions,

10   etc.).

Examples 5 and 6 show many areas of SWNT along

with MWNT and other carbon structures. Mo particles

ranged from <1-10 nm. In Example 4, mainly MWNT were

formed along with other structures of carbon. Mo

15   particles ranged from ~1-50 nm. Presumably, the

particles generated in Examples 5 and 6 were the right

size to promote SWNT growth over the other forms

possible. In Example 4, particle sizes favored growth of

MWNT and other forms.

20   **EXAMPLES**

Example 1

In a direct injection process, the catalyst

compartment was loaded with ~40 mg Molybdenum

hexacarbonyl [$Mo(CO)_6$] which has been ground to --100

25   mesh. The reactor was heated to $900^\circ C$ under an argon

flow. Argon was then replaced with CO at atmospheric

pressure at a flow of ~0.8 SLM and the catalyst was

injected.

10

The flow of CO was continued for 30 min. at 900°C, after which it was replaced by argon, and the reactor furnace turned off. After cooling to ambient temperature, the entire contents of the reactor including

5   the quartz wool plug which had been tared prior to the run, was emptied into a tared plastic bag. The quartz wool plug was blackened, but the yield of carbon growth (wgt C/wgt catalyst) was <1.

A specimen for Transmission Electron Microscopy

10 (TEM) was prepared by shaking the quartz wool plug in ethanol in a glass vial and ultrasounding the ethanol for ~2 min. This procedure dispersed the black particles from the quartz wool. A TEM grid was prepared by evaporating several drops of this dispersion onto a

15 carbon-coated copper grid.

Examination of the grid in the TEM showed a mixture of particles and carbon nanotubes, both MW and SW. Particles varied from ~1- several hundred nm and were shown to be Mo by dispersive X-ray analysis. The

20 MWNT ranged from ~4-10 nm diameter. Fishbone fibrils (10-50 nm diameter) were also formed.

Examination of the grid also showed several areas containing SWNT. Diameters ranged between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon

25 formed.

Example 2

The procedure of Ex. 1 was used to produce a mixture of Mo particles and carbon structures including

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both MWNT and SWNT. Catalyst charge [Mo(CO)$_6$] was ~8 mg.
SWNT yield was <50% of all nanotubes produced.

Example 3

The procedure of Example 1 was used to grow

5   SWNT using ~22 mg Co$_2$(CO)$_8$ as catalyst. TEM analysis
revealed Co particles to be the major component. MWNT
and SWNT ranging in diameter from 1-2 nm were also
formed. Estimated yield of SWNT was <25% of the
nanotubes formed.

10 **Example 4**

A simulated aerosol reactor (Fig. 1) was used
to produce SWNT. As the catalyst sublimed in the
vaporizer, the vapors were swept by the reactant gases
into the reaction section where they underwent immediate

15   thermal decomposition to Mo atoms and CO. It is
theorized that the Mo atoms aggregated and promoted
growth of carbon structures, including SWNT. These were
caught on the quartz wool plug.

Approximately 20 mg of Mo(C)$_6$ was loaded into

20   the vaporizer. Under argon at atmospheric pressure, the
reactor section was heated to 900°C while keeping the
vaporizer at ambient temperature. The argon stream was
then changed to CO @~0.8 SLM and H$_2$ @~0.08 SLM, and while
maintaining 900° in the reactor, the vaporizer

25   temperature was raised to 70°C. Over the course of the
run (1.5 hrs) the vaporizer temperature rose to 80°C due
to heat from the reactor furnace. The vapor pressure of
Mo(CO)$_6$ varied from 0.6-10 torr.

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TEM specimens were made by the same procedure as Ex. 1. TEM examination showed mainly very small particles of Mo ranging from ~1-10 nm. Also produced were amorphous carbon structures and MWNT with diameters

5   ~4 nm. SWNT with diameters ~1.5 nm were also produced, but in low yield.

Example 5

A procedure similar to Ex. 4 where ~20 mg $Mo(CO)_6$ was loaded in the vaporizer. With the reactor at

10   atmospheric pressure at 900°C, the vaporizer temperature was set at 40°C and CO was fed to the system @~0.8 SLM. Over the course of the run (1.5 hrs) the vaporizer temperature rose to 57°C. For this temperature span, the vapor pressure of $Mo(CO)_6$ ranged from 0.6-2 torr.

15   TEM examination showed mainly Mo nanoparticles 1-10 nm in diameter along with various carbon structures. These included amorphous carbon and MWNT with diameters of 4-10 nm. However, also produced were SWNT with diameters varying from ~1-3 nm. Estimated yield of SWNT

20   was <20% of the nanotubes produced.

Example 6

Using the procedure of Exs. 4-5, ~20 mg $Mo(CO)_6$ was vaporized at 38-41°C into the reactor zone which was set at 900°C. The feed gas comprised CO @0.8 SLM and H_2

25   @0.08 SLM and was fed at atmospheric pressure for 2.0 hrs. Vapor pressure of catalyst was nearly constant at ~0.6 torr.

13

TEM examination showed the presence of Mo

nanoparticles, many ~ 1 nm diameter. The usual amorphous

carbon and MWNT with diameters ranging from 4-10 nm were

seen. However, SWNT, 1-3 nm in diameter were also

5　produced at a yield of ~50% of the nanotubes produced.

Example 7

Examples 1-6 are summarized in Table I.

Precursor was obtained as a powder from ALFA/AESAR,

Research Chemicals and Materials. They were ground under

10　an argon blanket to ~-100 mesh.

RUN #	CATALYST PRECURSOR	FEEDSTOCK COMPOSITION	REACTOR TEMP	VAPORIZER TEMP	STEM	SWNT
1*	$Mo(CO)_6$	CO-100%	900°C	NA	Mix of particles and MWNT/SWNT	<50%
2*	$Mo(CO)_6$	CO-100%	900°C	NA	Same as above; X-ray showed no Fe	<50%
3*	$Co_2(CO)_8$	CO-100%	900°C	NA	Mostly particles, some SWNT strings	<25%
4**	$Mo(CO)_6$	CO-90% H_2-10%	900°C	70-80°C	Mostly particles, MWNT	trace
5**	$Mo(CO)_6$	CO-100%	900°C	40-57°C	Mostly particles and MWNT, some SWNT	<20%
6**	$Mo(CO)_6$	CO-90% H_2-10%	900°C	38-41°C	Particles, few MWNT, more SWNT	~50%

* Direct Injection Method
**Simulated Aerosol Method

Example 8

Ferrocene $(C_5H_5)_2Fe$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 9

Ferrocene $(C_5H_5)_2Fe$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at
5   an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

10   Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 10

15   Methylcyclopentadienyl manganese tricarbonyl $(CH_3C_5H_4)Mn(CO)_3$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a
20   mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm.
25   TEM estimate of the yield of SWNT was <50% of the carbon formed.

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Example 11

Methylcyclopentadienyl manganese tricarbonyl $(CH_3C_5H_4)Mn(CO)_3$ is substituted for the molybdenum

5   hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The

10   MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

15   **Example 12**

Cyclopentadienyl cobalt dicarbonyl $(C_5H_5)Co(CO)_2$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

20   Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several

25   areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

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Example 13

Cyclopentadienyl cobalt dicarbonyl $(C_5H_5)Co(CO)_2$
is substituted for the molybdenum hexacarbonyl in the
5   procedure of Example 6 at an appropriate vapor pressure
and temperature.

Examination of the grid in the TEM shows a
mixture of particles and carbon nanotubes, both MW and
SW. Particles vary from ~1- several hundred nm. The
10   MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several
areas containing SWNT. Diameters range between 1-2 nm.
TEM estimate of the yield of SWNT was <50% of the carbon
formed.

15   **Example 14**

Nickel dimethylglyoxime $(HC_4H_6N_2O_2)Ni$ is
substituted for the molybdenum hexacarbonyl in the
procedure of Example 2 at an appropriate vapor pressure
and temperature.

20   Examination of the grid in the TEM shows a
mixture of particles and carbon nanotubes, both MW and
SW. Particles vary from ~1- several hundred nm. The
MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several
25   areas containing SWNT. Diameters range between 1-2 nm.
TEM estimate of the yield of SWNT was <50% of the carbon
formed.

Example 15

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Nickel dimethylglyoxime $(HC_4H_6N_2O_2)Ni$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

5   Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several 10   areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

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CLAIMS:

     1.   A process for producing hollow, single-walled carbon nanotubes by catalytic decomposition of one or more gaseous carbon compounds comprising the steps of:

5   (1) forming a gas phase mixture of

     (a) a carbon feed stock gas comprising one or more gaseous carbon compounds, each said compound having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and

10   (b) a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions;

15   (2) conducting said decomposition reaction under decomposition reaction conditions and thereby producing said nanotubes.

     2.   The method defined in claim 1, wherein 50% or more of said carbon feedstock gas is carbon monoxide.

20   3.   The method defined in claim 1, wherein said carbon feedstock gas consists essentially of carbon monoxide.

     4.   The method defined in claim 1, wherein said decomposition reaction occurs at temperatures

25 between approximately 400°C and approximately 1300°C.

     5.   The method defined in claim 1, wherein said decomposition reaction occurs at temperatures between approximately 700°C and approximately 1100°C.

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6.   The method defined in claim 1, wherein said decomposition reaction occurs at a pressure range of approaching 0 p.s.i.g. through approximately 100 p.s.i.g.

7.   The method defined in claim 1, wherein

5 said gas phase metal containing compound is produced by vaporizing a liquid or solid phase metal containing compound.

8.   The method defined in claim 7, wherein said metal containing compound is vaporized into a

10 flowing stream of carbon feedstock, wherein the temperature of said flowing stream is between approximately 400°C and approximately 1300°C and wherein said flowing stream is at a pressure range of approaching 0 p.s.i.g. through approximately 100 p.s.i.g.

15   9.   The method defined in claim 1, wherein said gas phase metal containing compound is mixed with said feedstock by direct injection.

10.   The method defined in claim 1, wherein said gas phase metal containing compound is in the form

20 of an aerosol.

11.   The method defined in claim 1, wherein said gas phase metal containing compound is $Mo(CO)_6$.

12.   The method defined in claim 1, wherein said gas phase metal containing compound is $Co_2(CO)_8$.

25   13.   The method defined in claim 1, wherein said gas phase metal containing compound is a volatile iron compound.

14. The method of claim 13, wherein said volatile iron compound is ferocene.

15. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile manganese compound.

16. The method of claim 15, wherein said volatile manganese compound is methylcyclopentadienyl manganese tricarbonyl.

17. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile cobalt compound.

18. The method of claim 17, wherein said volatile cobalt compound is cyclopentadienyl cobalt dicarbonyl.

19. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile nickel compound.

20. The method of claim 19, wherein said volatile nickel compound is nickel dimethylglyoxime.

21. The method defined in claim 1, wherein said gas phase metal containing compound is produced by subliming a solid phase metal containing compound.

22. The method defined in claim 1, wherein said gas phase metal containing compound is produced by vaporizing a liquid phase metal containing compound.

23. Single-walled carbon nanotubes produced by catalytic decomposition of one or more gaseous carbon compounds comprising the steps of:

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(1)   forming a gas phase mixture of

(a)   a carbon feed stock gas comprising one or
more gaseous carbon compounds, each having one to six
carbon atoms and only H, O, N, S or Cl as hetero atoms,
5   optionally admixed with hydrogen, and

(b)   a gas phase metal containing compound
which is unstable under reaction conditions for said
decomposition, and which forms a metal containing
catalyst which acts as a decomposition catalyst under
10   reaction conditions;

(2)   conducting said decomposition reaction under
decomposition reaction conditions and thereby producing
said nanotubes.

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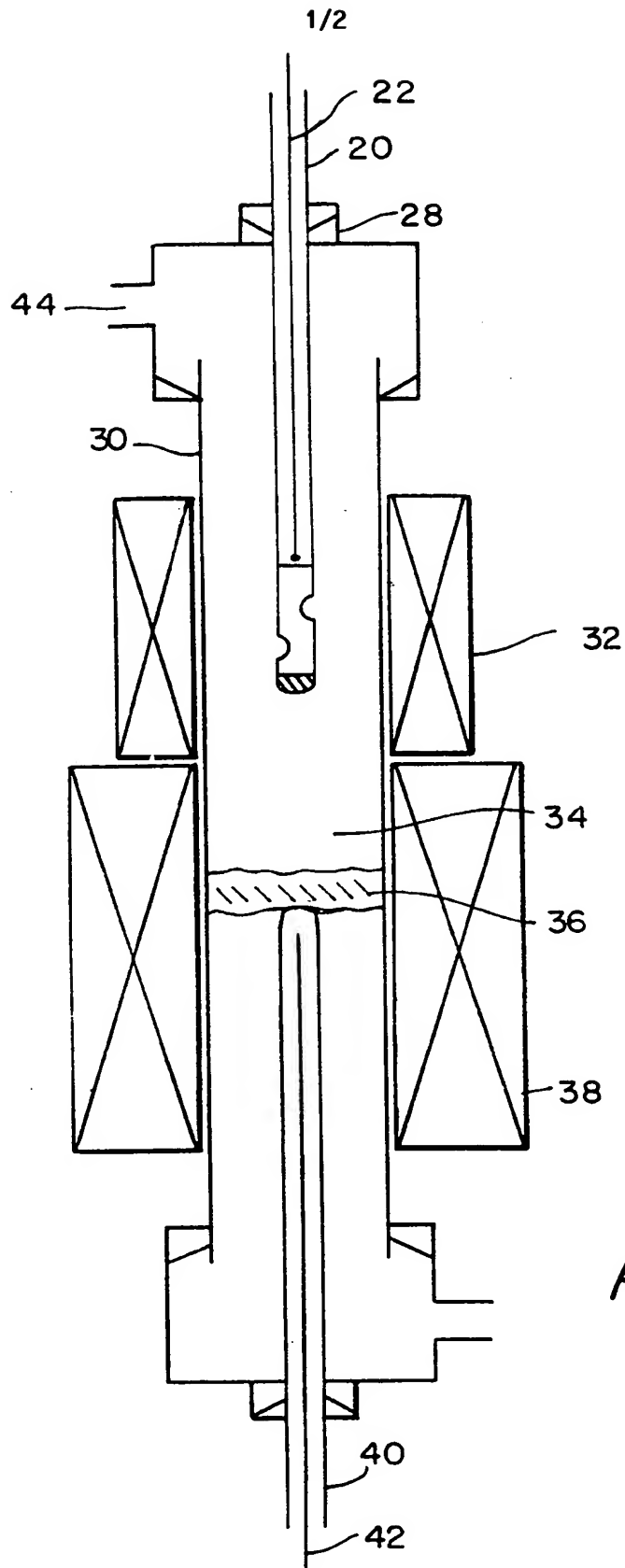
FIG. 1
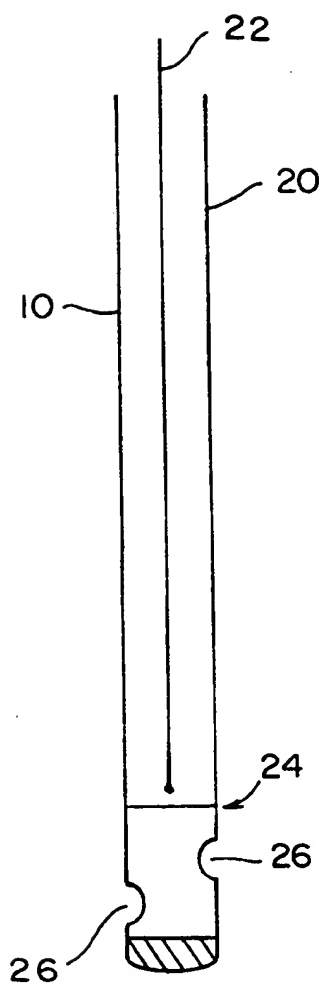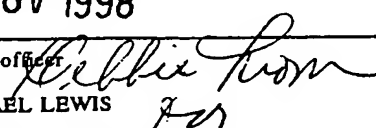
FIG. 2

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :D01F 9/12, 9/127; C01B 31/02
US CL :423/445B, 447.2, 447.3

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/445B, 447.2, 447.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,374,415 A (ALIG, et al.) 20 December 1994, column 5, line 15- column 6, line 22 and column 2, lines 47-65.	1, 4-7, 9, 13, and 22
X	JP 09-188,509 A (YOSHIKAWA) 22 July 1997, see entire document.	1, 4-5, 7-9, 13-14 and 21
Y	JP 06-322,615 A (IIJIMA et al.) 22 November 1994, see entire document.	1-22
Y	GB 2,248,230 A (KAWAGUCHI et al.) 04 January 1992, see page 4, lines 7-25 and page 7, lines 17-26 and page 8, lines 1-3.	1-22
X	KIANG, C-H. Carbon Nanotubes with Single-layer Walls. Carbon. August 1995, see page 903.	23

☐ Further documents are listed in the continuation of Box C.　☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"B"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 OCTOBER 1998	**1 9 NOV 1998**

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